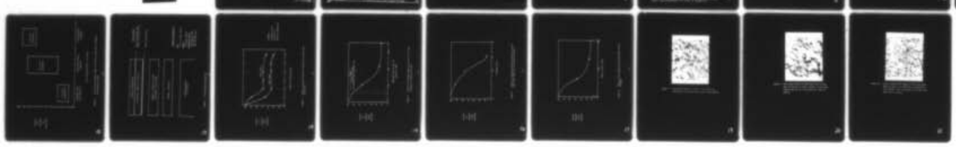
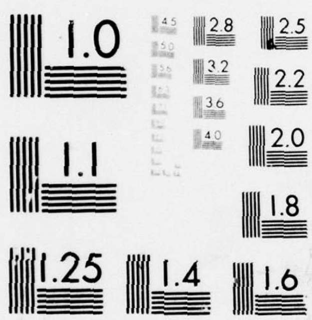
AD-A064 707 ROCKWELL INTERNATIONAL ANAHEIM CALIF AUTONETICS GROUP F/G 11/9
EFFECT OF HEAT AGEING AND RELATED PHENOMENON ON THE BLACK OXIDE--ETC(U)
FEB 77 W S DEFOREST, H V CONNELLY, J MARRO
UNCLASSIFIED X77-151/101 GIDEP-E072-0959 NL

1 OF 1
AD
AD 64707



END
DATE
FILMED
4--79
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

X77-151/101

EFFECT OF HEAT AGEING AND RELATED PHENOMENON ON THE BLACK OXIDE - EPOXY BOND

February 1977

22p.

By

W. S. DeForest, H. V. Connelly and J. Marro

X77-151/101

E072-0959, 347.15.00.00-C1-01

GIDEP, GIDEP

NEPCON '77 WEST
International Microelectronics Conference
Anaheim Convention Center
Anaheim, California

March 1-3, 1977

390 723

Rockwell International

Autonetics Group
3370 Miraloma Avenue
P.O. Box 3105
Anaheim, California 92803

JUN 24 1977

GOVERNMENT–INDUSTRY DATA EXCHANGE PROGRAM

DOCUMENT SUMMARY SHEET

Completion of Summary Sheet is Optional – Please Type All Information – See Instructions On Reverse

1. GIDEP INDEX NUMBER	2. DOCUMENT TYPE	3. ACCESS NUMBER
347.15.00.00-C1- 01	SPEC [ ] / NONSTD PART [ ] / TEST RPT [ ] / GEN RPT [X]	E072-0959

4. COMPONENT/PART NAME PER GENERIC CODE	5. ORIGINATOR'S DOCUMENT TITLE AND NUMBER
General Technical Data, Compatibility of Materials Reports	Effect of Heat Ageing and Related Phenomenon on the Black Oxide - Epoxy Bond X77-151/101

6. APPLICATION	7. MFR NOTIFICATION	8. DOCUMENT ISSUE (Month, Year)
Manufacturing	[ ] COPY OF REPORT [X] NOT APPLICABLE	February 1977

9. THIS DOCUMENT (SUPERSEDES) (SUPPLEMENTS) GIDEP INDEX/ACCESS NUMBER

None

	10 MFR AND H4 CODE NO.	11 MFR PART NO.	12 IND/GOVT STD NO.	13 TOTAL TESTED	14 EXCEEDED MFR CATALOG SPECS YES	NO
A	None	None Listed		N/A		
B						
C						

15	SPECS, ETC, REQD TO UTILIZE DOCUMENT	ENCL	SUBMITTED AS/WITH GIDEP INDEX/ACCESS NO.
A	None		
B			
C			

16 ITEM	TEST OR ENVIRONMENT	PER SPEC	SPEC PARAGRAPH METHOD/CONDITION	ENVIR CODE	NO. TESTED	NO. FAILED
	N/A					

17. SUMMARY

502.36.40.02-C1-CR
501.73.00.00-C1-CR
501.01.00.00-C1-CR

Peel testing was selected for evaluating the performance of the epoxy-black oxide bond under test conditions. This type of test was well suited because it was quantitative, repeatable and the test specimens could be laminated into flat pieces, resembling an MLB. It was established that the bond between epoxy prepreg and properly applied black oxide coating on copper foil is more heat resistant and stronger than the bond to the untreated foil. Thermal testing degrades the black oxide bond appreciably, but to a level no lower than the untreated foil. Black oxide, when properly applied, is suitable for use on any epoxy MLB provided it can be justified economically.

2

18. KEY WORDS FOR INDEXING

Multilayer Circuit Board; Copper Laminate

19. GIDEP REPRESENTATIVE	20. PARTICIPANT ACTIVITY
John Keary	Rockwell International, Electronics Operations, Anaheim, CA 92803

NOTE: COMPLETION OF A "DOCUMENT SUMMARY SHEET" BY THE PARTICIPANT IS NOT MANDATORY FOR DOCUMENT ACCEPTANCE INTO GIDEP. A SUMMARY SHEET WILL BE PREPARED BY THE GIDEP OPERATIONS CENTER FOR DOCUMENT SUBMITTALS RECEIVED.

DOCUMENT TYPE	(X) APPLICABLE FORM ENTRIES																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
SPECIFICATION	X	X	–	X	X	X	–	X	X	X	X	X	–	–	X	–	X	X	X	X
NONSTANDARD PART	X	X	–	X	X	X	–	X	X	X	X	X	–	–	X	–	X	X	X	X
TEST REPORT	X	X	–	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
GENERAL REPORT	X	X	–	X	X	X	–	X	X	X	X	X	–	–	–	–	X	X	X	X

BOX

1 *Enter GIDEP Index Number as established from "Codes for Establishing Index Numbers,"* Section 9, Policies & Procedures Manual. When GIDEP Index Number is identical with previous submittal, last two digits shall reflect next higher sequence number.

2 Identify document type by inserting letter X by appropriate descriptor.

3 Leave blank – entry will be completed by GIDEP Operations Center.

4 Enter standard nomenclature associated with 9–digit GIDEP Index Number selected from Section 9 for Box 1 entry.

5 Enter complete document title and number exactly as it appears on originator document.

6 Indicate application for which the device was used (*e.g., ground, missile, shipboard, spacecraft; refer to P&P Manual, Section 3*).

7 Device manufacturer must be notified of test results by a copy of report. Manufacturer approval of report is not required – include pertinent manufacturer correspondence with document submittal to GIDEP, check COPY OF REPORT entry. If document is of a general nature and a manufacturer is not identified, check NOT APPLICABLE; if document is a specification or a nonstandard part justification data package, check NOT APPLICABLE.

8 Enter month and year of document issue.

9 Delete either SUPERSEDES or SUPPLEMENTS. If document supersedes/supplements an existing GIDEP document, enter GIDEP Index Number and microfilm access number of appropriate document. If document neither supersedes nor supplements an existing GIDEP document, enter the word NONE.

10 Each line entry is used to differentiate between groups of parts. *All parts grouped as a single ITEM should be identical. Enter manufacturer abbreviation and* H–4 Code number listed in "GIDEP Vendor Abbreviation List." If manufacturer is not listed, enter the phrase SEE BOX 17; enter manufacturer's full name and division (if any) in Box 17. When there is more than one manufacturer, enter the phrase MULTIPLE, SEE BOX 17; make appropriate entries in Box 17. If a manufacturer is not specified, enter the word NONE.

11 Enter complete part number. Use open O for alpha letter O and use a Ø for numeric zero. If document pertains to a material or raw stock, enter the phrase STOCK MATERIAL. When there is more than one manufacturer, enter the phrase MULTIPLE, SEE BOX 17; make appropriate entries in Box 17. If a part number is not specified, enter NONE LISTED.

12 Enter standard part numbers such as the 1N and 2N – diode and transistor designators. For GIDEP purposes, any military assigned number is considered as a government standard part number. Whenever the situation occurs that a part or component has (1) manufacturer P/N, (2) contractor P/N, (3) industry std P/N, and (4) a government std P/N, the manufacturer and industry std P/N's are entered in Boxes 11 and 12 respectively. The government std P/N is entered as a parenthetical expression following the originator's report title in Box 5; the agency name must accompany the P/N, e.g., NAVORD 2883084. The contractor P/N is not used.

13 Enter total quantities of each part type or group tested. If any control samples were included in the number of parts tested, use the footnote symbol 1/ accordingly, and enter applicable information in Box 17. If not applicable, enter N/A.

14 Check entry as applicable.

15 Identify applicable specification(s), standard(s), control drawing and acceptance test procedure required for document interpretation (e.g., MIL–STD–202). If reference is enclosed, check ENCL column. If reference was previously submitted as a GIDEP document, list GIDEP Index Number and microfilm access number in the SUBMITTED AS/WITH GIDEP INDEX/ACCESS NO. column. When a military document is listed for use in Box 16 (PER SPEC column), enter REFERENCED IN BOX 16 in SUBMITTED AS WITH––– column. If a document is not enclosed or referenced, enter NONE in SPECS ETC, REQD TO UTILIZE DOCUMENT column.

16 ITEM. This entry is used in conjunction with Boxes 10 and 13. For documents that report test results on one device (*single line entry*) in *Box 10 and total number listed in* Box 13 were subjected to TEST OR ENVIRONMENT entry, enter ALL. When a test sample or subset of total devices is less than total of Box 13, enter designator A1 to identify which of selected parts were tested to environment specified. Each different subset for subsequent test environments will require a separate line entry and identified A2, A3, etc. If not applicable, leave blank.

TEST OR ENVIRONMENT. *Enter the type of test or environment.* An entry is required for each test or environment that test sample was subjected (e.g., salt spray, vibration, shelf life). If not applicable, enter N/A.

PER SPEC. Enter the letter from Box 11 which identifies the applicable reference.

SPEC PARAGRAPH METHOD/CONDITION. Enter specific military document(s) listed in Box 15 and test method or condition used as part of reported test(s) (e.g., if a Vibration Test to MIL–STD–202 was recorded as TEST OR ENVIRONMENT entry, associated entry would be Method 214). If there are none, enter NONE.

ENVIR CODE. Enter the single symbol code for environmental exposure as defined in "Codes for Establishing Numbers," Section 9, Policies and Procedures Manual (e.g., C – salt spray; V – vibration; % – shelf life).

NO. TESTED. *Enter total number of test samples exposed to specific test or environment. If not applicable, enter N/A.*

NO. FAILED. Distinguish between a failure to satisfy requirements and an intentional test to failure, such as burst test. Note the latter type failure by indicating the design limits vs the point of failure. (A test sample which bursts – breaks, arcs – above specification requirements is not a failure.) If not applicable, enter N/A.

17 Briefly summarize test results or material detailed in text of the document. Include any pertinent details or comments required for proper interpretation of material presented (e.g., peculiar environmental capabilities, unique electrical characteristics that may be "state–of–the–art," or characteristics that restrict part usage to particular applications or any other details that may aid a prospective user of the part.

18 Enter appropriate words or phrases that enhance information retrieval on subject matter(s) presented in document. The document is referenced in the data bank for retrieval purposes according to each key word. Do not use abbreviations or words that are part of the GIDEP generic dode standard nomenclature listed in Box 4. Key word phrases are limited to 60 total characters and blank spaces. Separate key words and/or phrases with commas.

19 Enter signature or name of GIDEP Representative.

20 Enter name, city and state of participant activity or corporation and division submitting the document.

NOTE: USE EITHER GIDEP FORM 1B OR 1C FOR CONTINUATION PAGE AS REQUIRED.

Table of Contents

EFFECT OF HEAT AGEING AND RELATED PHENOMENON ON THE BLACK OXIDE - EPOXY BOND

by

W. S. DeForest, H. V. Connelly and J. Marro

Introduction

Black oxide films on copper foil have been used to increase the strength and heat resistance of the bond between foils and laminates since the early days of circuit board manufacture. Eisler[1] mentioned its use in 1959 for this purpose. Before that, black oxide was used as a decorative finish on copper and brass. The oxide is formed by immersing the part in a hot alkaline solution of sodium chlorite. Commercial solutions for oxiding copper vary considerably in concentration and to lesser extent in composition. In-house formulations can also be prepared[2] and are becoming more widely used. All data herein, however, were gathered from parts oxided in a commercial formulation.

The black oxide process is relatively simple (Table I) and the bond is a considerable improvement over bare copper (Figure 1). It has not, however, gained universal acceptance for several reasons:

1. black oxide adds additional processing costs;
2. unless properly controlled, parts will be lost in the electroless plating line.

In the latter instance, thick layers of black oxide prevent actual bonding of the prepreg to the copper. After the through hole is drilled, the black oxide interface is exposed to the chemical processing solutions through the electroless copper. Strong mineral acids, particularly the hydrochloric acid in the catalyst predip, will selectively remove the oxide at the interface in the hole and leave a hollow zone between the prepreg and foil. Because the surface foil covers this type of defect, it will go undetected until the part is etched or cross-sectioned after plating.

---

[1] P.Eisler, The Technology of Printed Circuits, Heywood and Company, London, England, 1959

[2] F.P. Darmory, "Polyimide Laminating Resin for Multilayer Printed Wiring Boards," Insulation/Circuits, Vol. 21, No. 10, October 1974

Regarding cost of application, there are many parts that can perform adequately without the oxide which would render it only an additional expense.

In spite of these objections, the use of black oxide in one form or another is on the increase. Some users of MLBs have gone so far as to require black oxide in procurement specifications. The reason for this resurgence is not clear, but is probably related to the increased use of MLBs by the industry. The incidence of wave soldering defects relating to the laminate - copper bond is far greater with MLBs than with single or double-sided boards. The use of black oxide on the internal layers will reduce this type of defect, as many companies have found.

At Rockwell International, the black oxide process was evaluated for ground support equipment and found to be a definite improvement over the untreated foil. Wave soldering losses were reduced significantly and the additional time required to apply the oxide and control the solutions are cost effective. Because of the success with ground support equipment, the process was investigated for use on high reliability airborne equipment. Salient portions of the results are reported herein.

THERMAL RESISTANCE TESTING

Peel testing was selected as the means of quantitatively evaluating the performance of the epoxy-black oxide bond under test conditions. This type of test was well suited because it was quantitative, repeatable, and the test specimens could be laminated into large flat pieces that somewhat resembled an MLB. (See Figure 2). The actual peel testing was performed on one inch wide strips cut from the larger pieces.

Specimens used in this test were prepared with a commercial oxidizing solution. Initial peel test values ranged between 6.3 and 8.6 lbs/inch with an average value of 7.3 lbs/inch. Values in this range are not uncommon and are considerably better than untreated copper foil as indicated in Figure 1.

Peel testing was performed at ambient temperature at a rate of 2 inches/ minute peel.

Solder Cycling

Black oxide specimens had good resistance to solder float cycles as shown in Figure 3. The most drastic change occurred after the first cycle at 285C and the higher solder temperature did the most permanent damage to the bond. In no instance did the specimens blister or delaminate. At 246C, two cycles were required before drastic changes in adhesion were noted. It should be noted that the adhesion was still better (>3.5 lbs/inch) than is normally obtained with untreated copper before any thermal testing (1 to 3 lbs/inch).

Hot Oil Immersion (Solder Flow)

At an oil temperature of 200C, small parts such as the test specimen will undergo solder flowing after about 15 seconds immersion. An 8-layer MLB would typically require 35 seconds and very large, thick boards of 18 to 20 layers would require 55 seconds. The difference in time required for solder flow is directly proportional to the mass of the parts. Solder plating will melt around the same temperature each time, but it simply takes a longer immersion time for the heavier parts to get that hot.

In Figure 4, the effect of immersion time in hot oil at 200C on the retained bond strength is shown. Note that the shape of the curve is similar to that obtained with the solder float cycling. No blistering or other visible signs of bond degradation were detected. This bond degraded to a point lower than that observed with the solder float tests. Certainly, board losses from laminate defects are much less with the hot oil than with the molten solder because of the lower temperature and heat capacity of the oil. However, prolonged exposure to hot oil can seriously degrade the bond while causing no visible laminate defects. As a precaution, solder flow cycles in hot oil should be kept to a minimum in time and temperature.

Thermal Cycling

Thermal cycling significantly degraded the bond strength as indicated in Figure 5. The cycles were extreme (Table II), consisting of total immersion in liquid media at -75 to 175C. Shock was severe, particularly considering the small mass and large surface area of the specimens.

Even under these conditions, the oxide-epoxy bond fared well. The adhesion degraded after 15 cycles to that of a specimen with untreated foil that was not cycled (2.8 lbs/inch). Note the resemblance to the results obtained in the previous tests. The similarity of the shape of the curve in Figure 5 to those in Figures 3 and 4 could indicate that the bond was degrading in a similar manner.

Heat Ageing

A life cycle test conforming to MIL-STD-202E, method 108A, test condition D, was performed on test specimens. The parts were heat aged for 1000 hours at 125C. A 10-second solder float at 246C was used to simulate assembly. Specimens were removed at 336 and 667 hours and tested. The results, plotted in Figure 6, show a gradual degradation to a value within the range of untreated copper (3.1 lbs/inch) and somewhat resembles the previous curves. Untreated foil specimens were also tested and degraded from 2.3 to 1.3 lbs/inch which is a higher percentage (57%), but less strength overall.

BOND STRENGTH IMPROVEMENT

It is evident that the black oxide improves the bond strength and that it has at least two distinct components which provide adhesion:

(a) adhesion from the tiny oxide fibers on the flat copper surfaces (Figure 7);

(b) adhesion from the macroroughened areas in the foil (Figure 8).

Bond Strength Improvement (continued)

The existance of component (a) is indicated by Figure 9 which shows an oxide surface after peel testing. Note that nearly every fiber has been removed with the prepreg. In the flat areas, these fibers provide additional bond strength that would not be expected with untreated foil. (See Figure 1)

Bond strength from component (b) would be expected with or without black oxide and would range from one to three pounds per inch. The black oxide process may also further roughen the surface as indicated by Figure 10 to slightly improve adhesion.

From the general shape of the curves in Figures 3 through 6, the adhesion from component (a) is most affected by the thermal excursions in the testing. In all instances tested, the value remaining after the thermal resistance test was similar to the value noted for untreated copper (Figure 1) or component (b). The loss of strength noted initially for component (a) would be the result of mechanical stresses on the brittle fibers from thermal contraction and expansion.

PASSIVATION AND CLEANING EFFECTS

In addition to strengthening the prepreg-circuitry bond, the oxide treatment cleans and passivates the copper which reduces blistering and delamination at elevated temperatures. Immersion in a hot alkaline oxidizing solution removes residues and volatile materials from both the epoxy and copper. Unclean copper will not form an oxide and copper colored areas can readily be seen in contrast to the oxidized areas. Stripping and reoxidation processes are simple and routine. Unpassivated copper promotes blister formation at or above 175C according to Schuessler [1] and black oxide was recommended as one method of passivation. The reaction cited involved the formation of water through the interaction of unpassivated copper and the polymer molecules in intimate contact with the surface at elevated temperature. Steam from the moisture separated the copper and epoxy. Blistering from this source should

---

[1] P. Schuessler, "Preventing Delamination of Circuit Boards and Flexible Circuits," Insulation/Circuits, Vol. 20 No. 7, July 1973.

Passivation and Cleaning Effects (continued)

not occur during lamination because the pressure is sufficient to keep the water in the liquid state. At elevated temperatures and ambient pressure, steam can form blisters. Such blisters, when opened, will reveal a very clean copper surface, a small amount of moisture which quickly evaporates, and sometimes, a fine white powder.

Regardless of the mechanism, blistering was prevalent with the untreated specimens tested at or above 175C and quantitative data were difficult to obtain. At 125C, the untreated specimens did not blister as indicated in the Heat Ageing Test.

It should not be inferred that an MLB will necessarily tend to blister or delaminate upon short term exposure to temperatures of 175C or more without black oxide on the internal layers. There are several differences to consider:

1. The test specimens reached thermal equilibrium more rapidly with the test medium than an MLB because of the small mass (about 50 grams) and large surface area (36 in^2/side) of the specimens. The bond had to endure more time at the test temperature than an MLB internal layer bond which was thermally insulated by several layers of epoxy.

2. Because of the rapid temperature rise, thermal shock was greater on the test specimen than an MLB.

3. The internal bonding surface of the test specimens was all copper. There was no areas where the prepreg could bond to the base laminate. The epoxy-to-epoxy bond is much stronger and more heat resistant than the epoxy bond with untreated copper.

CONCLUSIONS

The bond between epoxy prepreg and a properly applied black oxide coating on copper foil is more heat resistant and stronger than the bond to the untreated foil. Thermal testing degrades the black oxide bond appreciably, but to a level no lower than the untreated foil. Black oxide, when properly applied, is suitable for use on any epoxy MLB provided it can be justified economically.

REFERENCES

1. P. Eisler, The Technology of Printed Circuits, Heywood and Company, London, England, 1959.

2. F. P. Darmory, "Polyimide Laminating Resin for Multilayer Printed Wiring Boards," Insulation/Circuits, Vol. 21, No. 10, October 1974.

3. P. Schuessler, "Preventing Delamination of Circuit Boards and Flexible Circuits," Insulation/Circuits, Vol. 20, No. 7, July 1973.

Table I

Typical Application Sequence
for
Black Oxide

1. Scrub with pumice and rinse.
2. Light acid etch (optional) and rinse.
3. Immerse in commercial oxidizing solution.
4. Rinse thoroughly and dry.
5. Bake 250F for 30 to 45 minutes.
6. Laminate.

Table II

Thermal Cycling Test

<u>One Cycle</u>

1. Total immersion in a cold liquid at -75C.
2. Total immersion in a hot liquid at 175C.

Note: Transfer times in air between immersions to be less than 10 seconds.

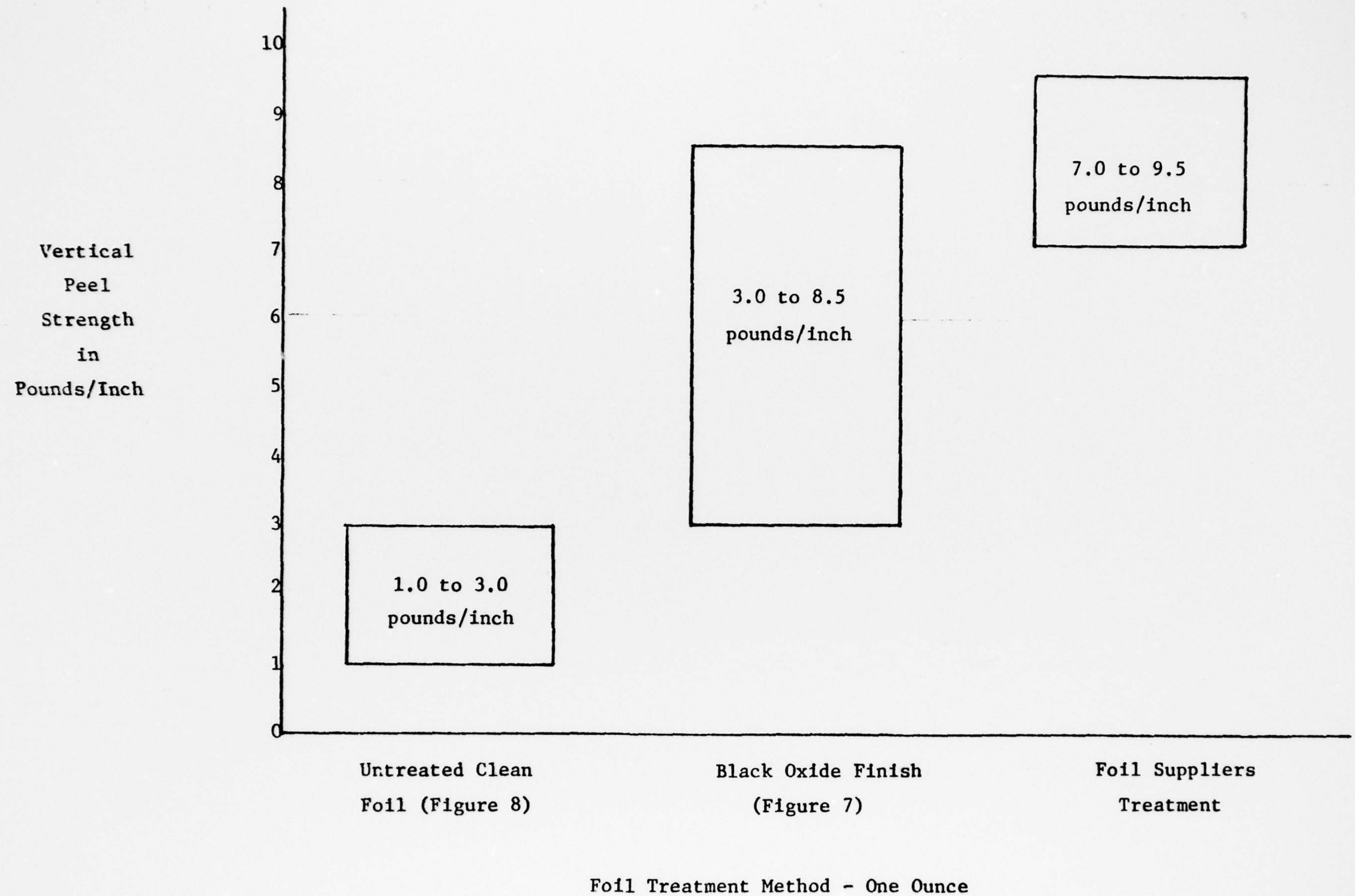


Figure 1. Typical bond strength ranges for various copper foil treatments found during testing.

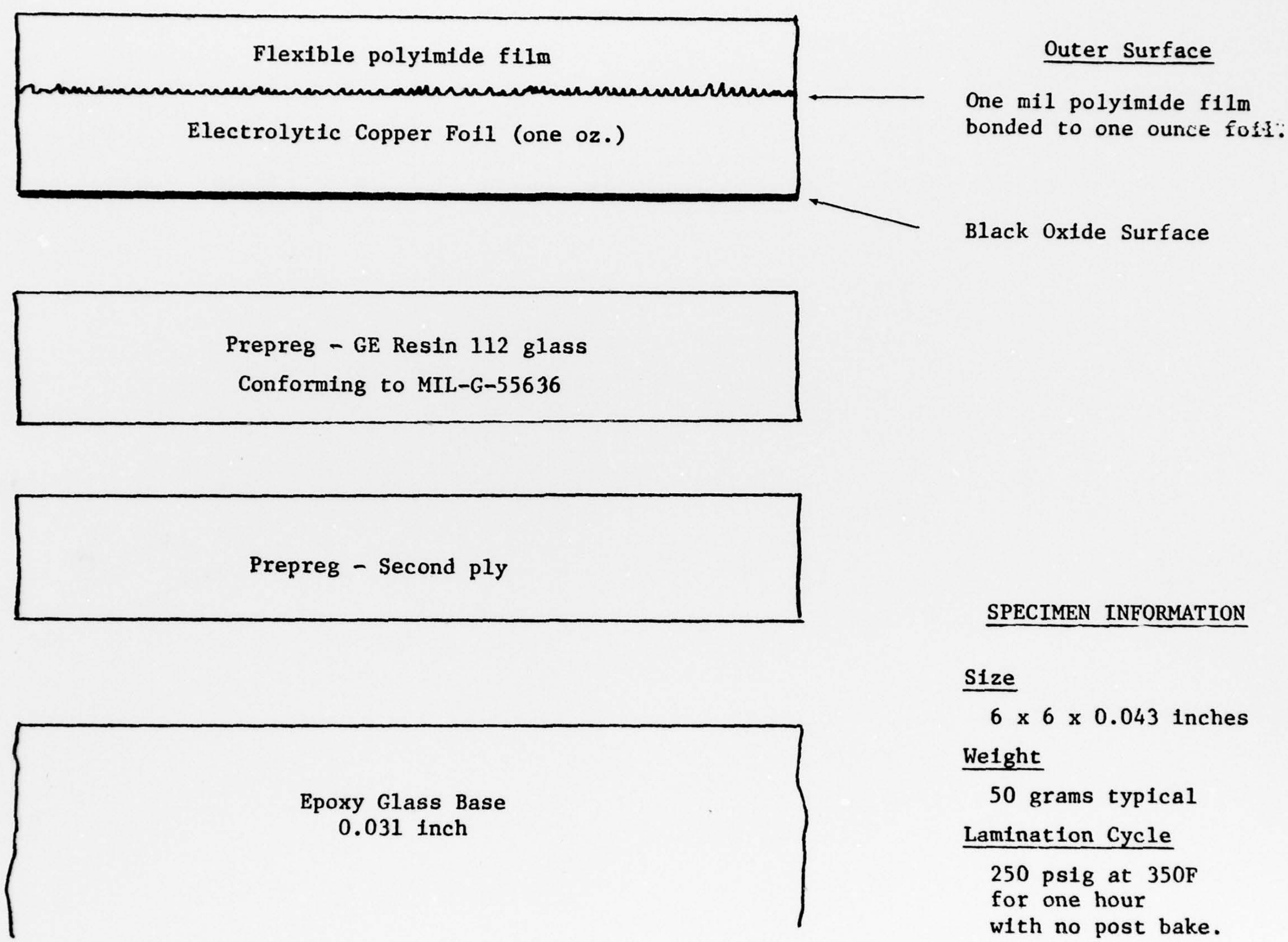
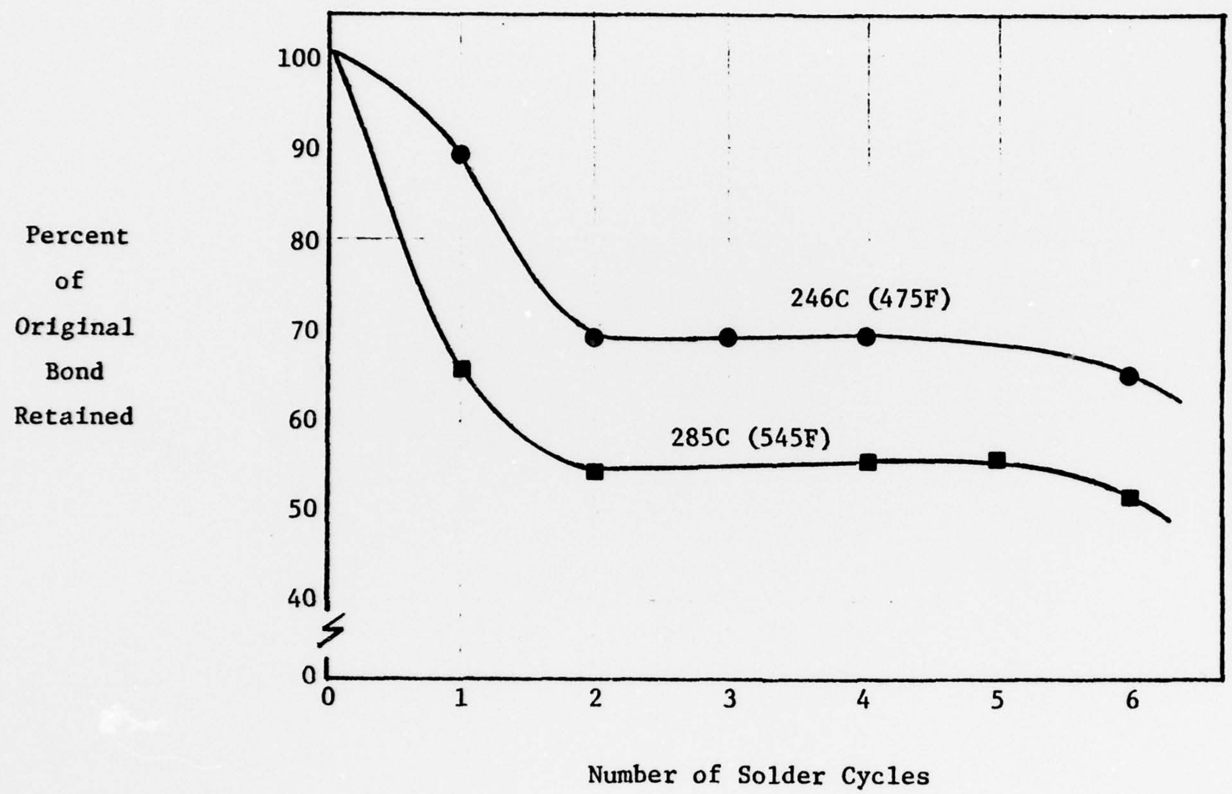


Figure 2. Test specimen description



1 Cycle

10 second float
and cool to
ambient temperature

Figure 3. Effect of repeated solder cycling on the black oxide epoxy bond.

14

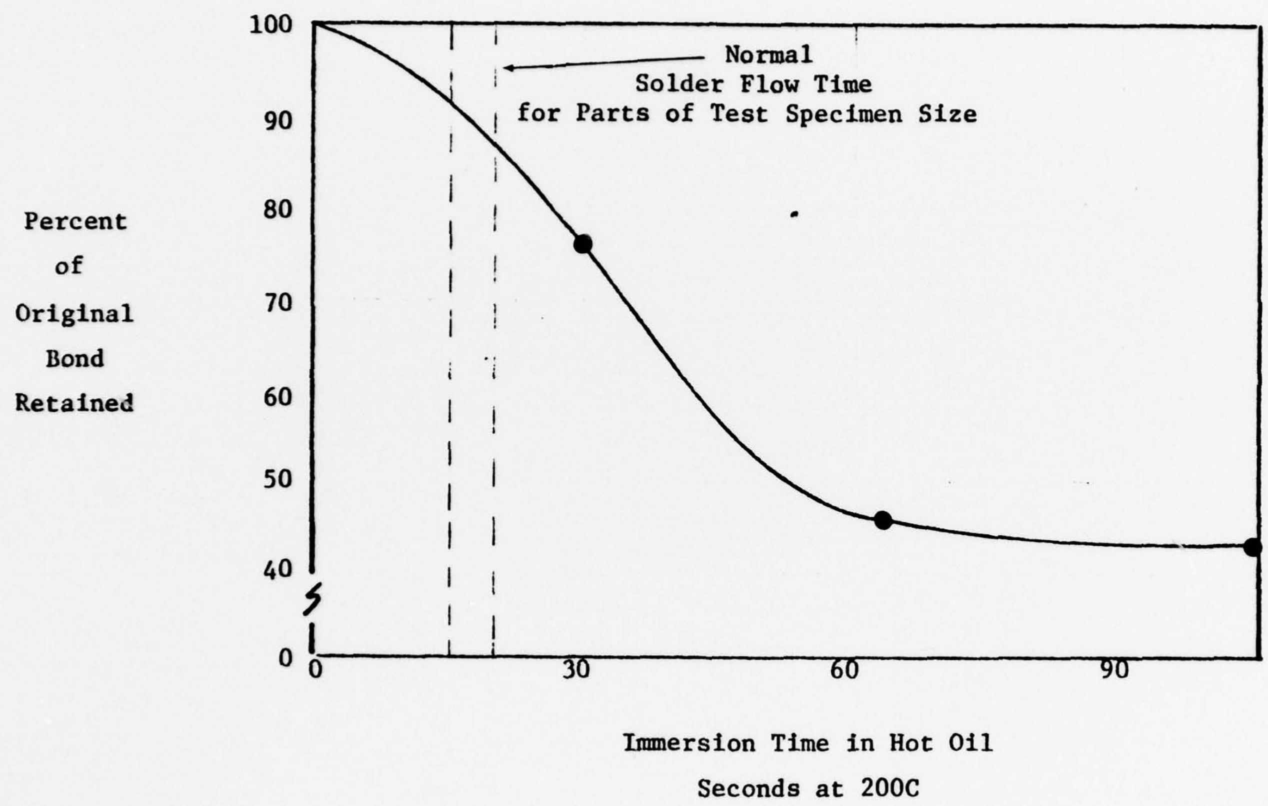


Figure 4. Effect of prolonged immersion in hot oil on bond strength of epoxy-black oxide.

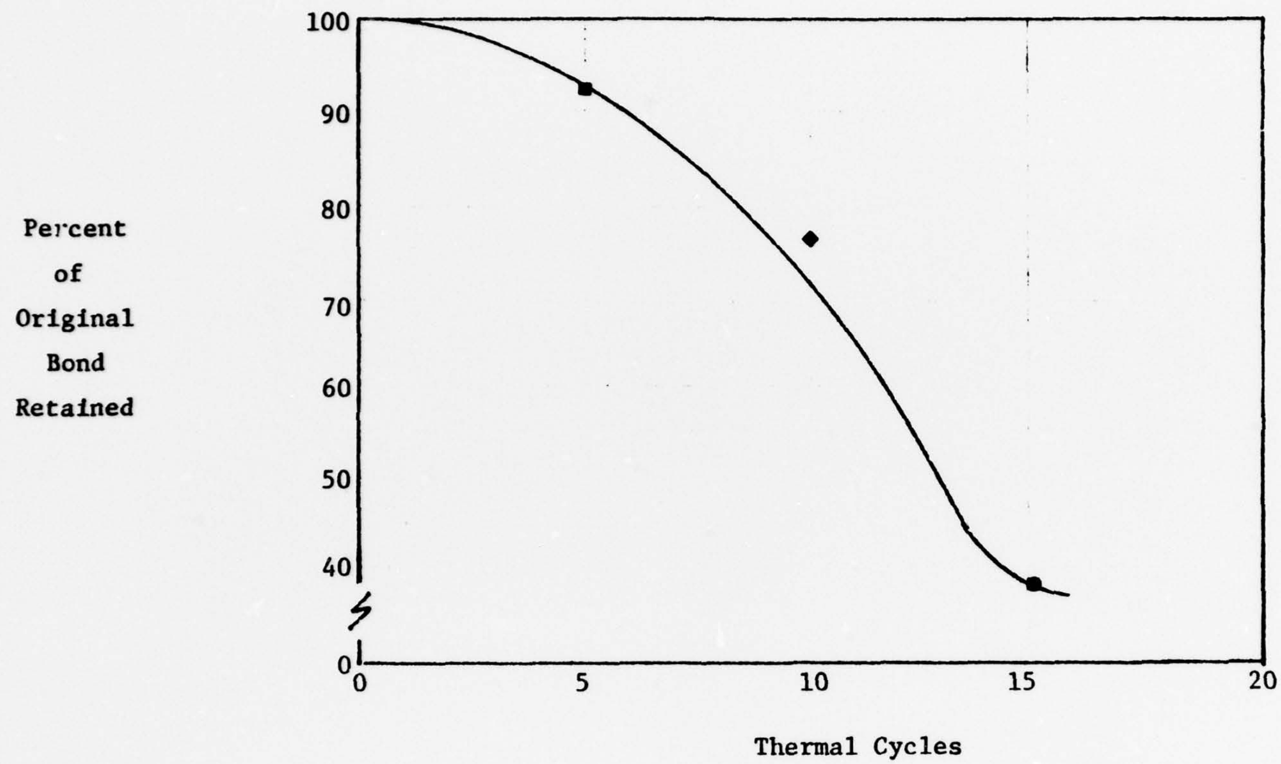


Figure 5. Effect of continuous thermal cycling in liquid media (See Table II) on the bond strength.

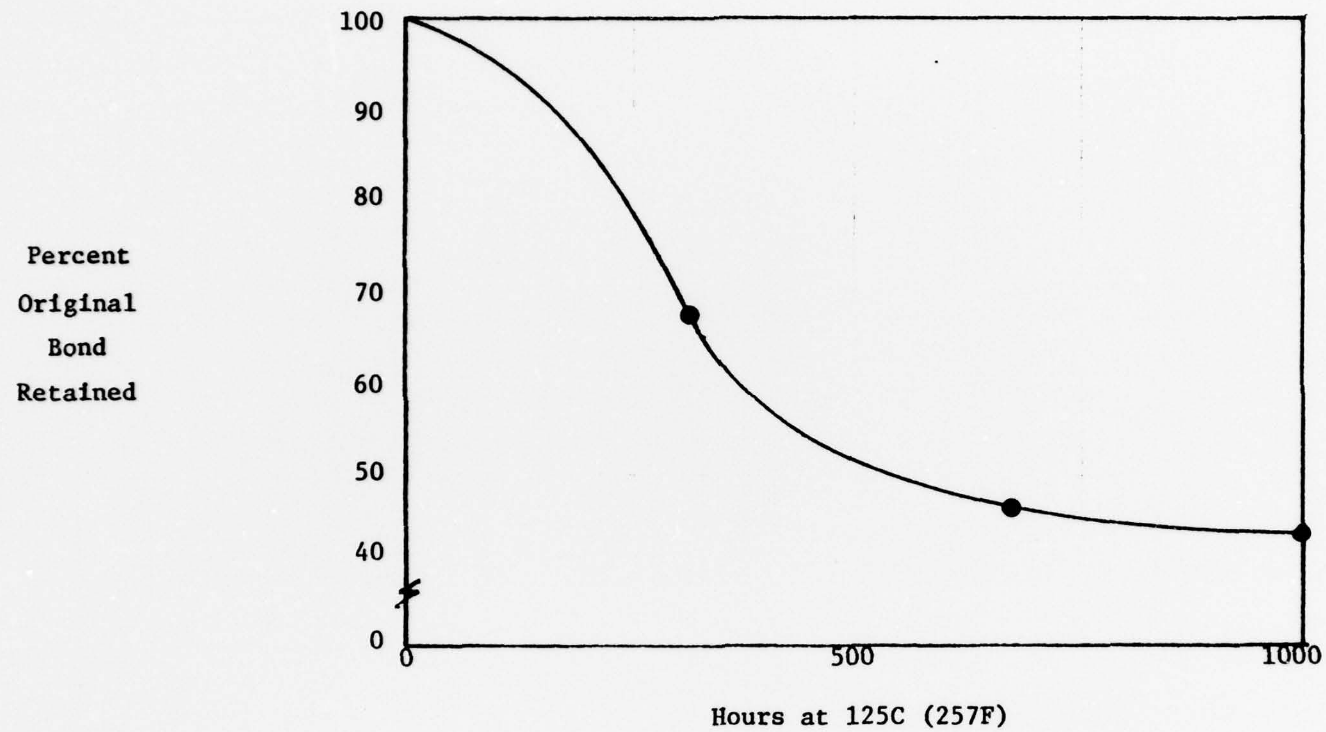


Figure 6. Effect of heat ageing per MIL-STD-202E on bond strength.

Figure 7. Black oxide surface at 5000X. The oxide is in the form of tiny fibers which bonds to the prepreg.

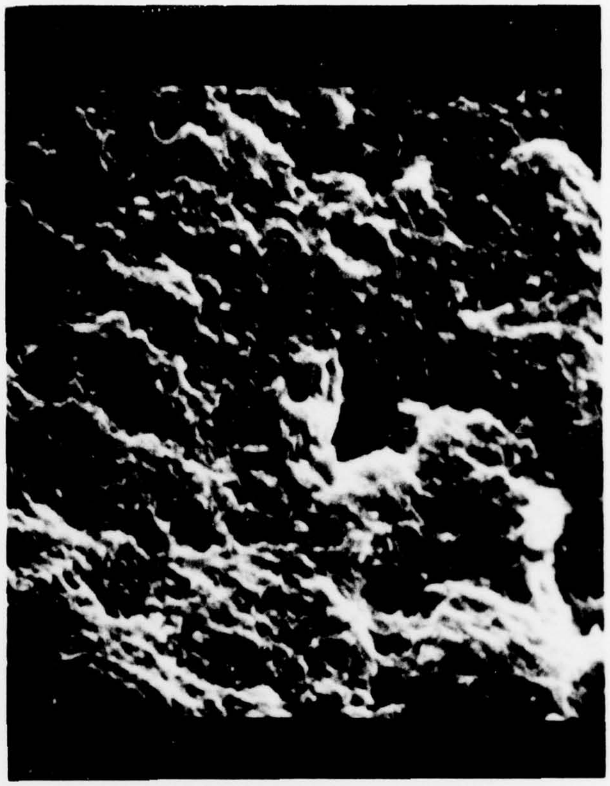


Figure 9. Black oxide surface at 5000X after peel testing Note the absence of fibers, (Figure 7) which were removed when the foil was peeled away from the prepreg.

Figure 10. Copper surface after removal of the black oxide shown in Figure 7 by immersion in hydrochloric acid (5000X). Note the absence of the many flat areas seen in Figure 8.